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Effects of Metal-Organic Frameworks on CO2 Solubility in Aqueous Amine Solutions

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ABSTRACT— Amino-functionalized Zr-MOF was synthesized with solvothermal method and characterized by X-ray diffraction (XRD), infrared spectroscopy (IR), thermogravimatric analysis (TGA), transmission electron microscopy (TEM) and nitrogen physisorption measurement (BET) techniques. The solubility of carbon dioxide in the aqueous solution of 40wt% N-methyldiethanolamine MDEA was measured by using a static high pressure equilibrium cell at temperatures of 303.15, 313.15, 323.15, and 333.15 K, and carbon dioxide pressures up to 2300 kPa. Then these measurements were repeated for aqueous solution of 40wt% MDEA with 0.2 wt% of UiO-66-NH2. Comparing the results showed that addition of UiO-66-NH2 nanoparticle to amine solution increases the CO2 solubility up to about 20%.
KEYWORDS: Carbon Dioxide, Amine, MDEA, UiO-66-NH2, MOF, Solubility

Introduction

Removing of acid gases such as CO_2 and H_2S from natural gas is one of the significant operations in gas processing that named gas sweetening. There are different methods for CO_2 separation from natural gas. The most widely used method is absorption in aqueous solutions of alkanol amines such as monoethanolamine (MEA), diethanolamine (DEA), Triethanolamine (TEA), diglycolamine (DGA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA). The chemical absorbing reaction of carbon dioxide gas by alkanol amines is exothermic reaction that can be happened at room temperature and reversed at high temperatures [1]. MDEA is the most important alkanol amine in industries and refineries, because of selective removal of H_2S from gases that containing both CO_2 and H_2S like some natural gases, stable structure and does not degrade readily. MDEA used for the first time by Frazier and Kohl [2]. Another method for removing CO_2 from natural gas is separation by porous materials. Some traditional adsorbents such as zeolites and activated carbons have high adsorption capacity but their regeneration is very difficult at low temperatures. Recently metal-organic frameworks (MOFs) have attracted attention of researchers. MOFs consist of three dimensional networks made by metal nodes and organic linkers. These materials have high porosity, large surface area, flexible framework and selectivity. Some MOFs have specific characteristics like thermal, mechanical and water stability [3-6]. In this work, although both high CO_2 capacity and high CO_2 selectivity are necessary, the important feature is water stability. So, we choose Zr based MOF because of their thermal and aqueous stability [7, 8]. UiO-66 is Zr-based cluster formed by cubic structure of cationic $Zr_6O_4(OH)_4$ nodes and 1,4-benzenedicarboxylate linkers (BDC) [9]. To increase the UiO-66 CO_2 storage capacity, there are different methods. One of them is adding functional group. Amine functionalized UiO-66, UiO-66-NH$_2$, was selected and prepared by solvothermal method [10]. The effect of adding UiO-66-NH$_2$ nano structure MOF, to MDEA solution on increasing of CO_2 solubility in MDEA perused and the isotherms were obtained in different temperatures.

2. Experimental
2.1. Material
Dimethylformeamide (C_3H_7NO), 2-aminoterephtalic acid ($C_8H_7NO_4$) and Methyldiethanolamine ($C_5H_{13}NO_2$) with purity of more than 99% were purchased from sigma-Aldrich. Zirconium chloride ($ZrCl_4$) 99%, Hydrochloric acid (HCl) 37% and ethanol (C_2H_6O) 99.5% were purchased from Merck. CO_2 was obtained from Roham Gas Company with 99.5% purity.

2.2. Synthesis of UiO-66-NH$_2$
UiO-66-NH$_2$ was synthesized according to a procedure reported by Katz et al [11]. First 125 mg (0.54 mmol) $ZrCl_4$, 5 mL of DMF and 1 mL of concentrated HCl was taken in 8 dram vial (30 mL) and being sonicated for 20 minutes until fully dissolved. Then 134 mgr (0.75 mmol) 2-aminoterephtalic acid (ligand) and 10 ml of the DMF were added and the mixture was sonicated for 20 minutes after that was heated at 120°C for 24 hour. The resulting solid was collected by filtration, and the product was washed first with DMF (2 x 30 mL) and then with EtOH (2 x 30 mL). The sample was washed and filtered for several times to remove all residual materials and solvent. For activating, first was heated to 90 °C under vacuum then the temperature increased up to 150 °C for 3 hours.

2.3. Preparation of solution
The 0.4 mass fractions of MDEA 99% were mixed by 0.6 mass fractions of deionized water to obtaining 40 *wt*% MDEA (equal to the concentration of MDEA in industry). The nano fluid was achieved by adding 0.2 mass fractions of UiO-66-NH$_2$ to MDEA

40 *wt*% solution and degasing in water-filled ultrasonic bath for 20 minutes. Zeta potential Measurement and XRD showed that UiO-66-NH₂ particles are stable in aqueous 40wt% MDEA.

3. Characterization
3.1. XRD
XRD patterns of UiO-66-NH₂ are illustrated in Figure 1. These patterns contained predictable peaks of UiO-66 at 2θ = 7.34°, 8.48° according to the literatures [12, 13]. This work needs kind of MOFs that is water stable [14-16]. For demonstrating of UiO-66-NH₂ water stability, it was immerged in water for 10 days. XRD pattern of this sample (UiO-66-NH₂ after 10 days mixing with water) is also shown. The figure shows that its crystal structure did not change.

3.2. IR spectroscopy
The IR spectrum of UiO-66-NH₂ is shown in Figure 2. The band at 762 cm⁻¹ is appointed to the C-C vibrational mode and the bands at 1434 cm⁻¹ and 1570 cm⁻¹ assigned to C-C stretch in aromatic compounds. The peak in 1262 cm⁻¹ is referred to C–N stretch band. The absorption band at 1570.73 cm⁻¹ demonstrated the reaction of –COOH with Zr⁴⁺. The C–H stretch band is observed at 2975 cm⁻¹ .The primary aromatic amino group displayed two peaks with lower intensities at 3370 cm⁻¹ and 3475 cm⁻¹ indicated symmetric and asymmetric vibrations of NH₂ groups[12, 13, 17].

3.3. TG analysis
To examine the thermal stability of the UiO-66-NH₂, thermo- gravimetric analysis (TGA) was carried out and the results are shown in Figure 3. It can be seen that this porous structure releases its free molecules and solvent in the temperature ranges of 30-140°C. The dehydroxylation of OH⁻ is done at 200- 300°C. This MOF started to decompose above 350°C and decomposed completely at temperatures close to 560°C. So, UiO-66-NH₂ is stable up to 350°C.

3.4. TEM morphology
Figure 4 shows TEM micrograph of UiO-66-NH₂. As seen, the porous structure of amino-Zr-MOF presents symmetrical crystals and the average particles size is below 100 nm.

3.5. BET Surface area
The BET surface area of UiO-66-NH₂ at 200°C is 842.1127m²/g and Langmuir Surface Area is 1113.38 m²/g. The pore volume of this sample is 0.401838 cm³/g, the pore size is 19.0871 Å and average particles size is about 71.249 Å.

3.6. Zeta potential
Figure 5 shows the zeta potential diagram for the solution of 0.2 wt.% UiO-66-NH₂ in 40wt% MDEA. The measured zeta potential for this nanofluid is -26.5 which confirmes good stability of colloidal dispersions.

4. CO₂ solubility Measurements
4.1. Testing procedure and calculation method
CO₂ solubility Measurements were conducted on a system that is shown in Figure 6. A stainless steel reactor (total volume: about 290 mL) was heated by a water circulating bath (Lauda model Proline P12) and was mixed by magnetic stirrer at the bottom of reactor. The reactor consists of valves for the ininjection of feed and a connection to a vacuum pump. The solution temperature was recorded by a calibrated thermocouple inserted to the cell. The pressure of the cylinder and gas container was measured with pressure transmitter sensor (Druck model PTX 1400).

First, the reactor was evacuated by vacuum pump and the certain amount of solution was injected to the reactor. the reactor`s temperature was set at the desired value. After getting equilibrium the pressure is recorded (P_V). A certain amount of CO₂ was introduced into the equilibrium cell from gas container.

$$n_{CO_2} = \frac{V_c}{RT_a}\left(\frac{P_1}{Z_1} - \frac{P_2}{Z_2}\right) \tag{1}$$

Where V_c is the volume of the gas container, Z_1 and Z_2 are the compressibility factors corresponding to the initial and final pressure (P_1 and P_2) in the gas container before and after transferring the CO₂ and T_a is the temperature of ambient. After gas injection the stirrer was switched on at a constant speed. When the pressure of the equilibrium cell (P_{Total}) had been consistent and steady for normally about 3-4 hours the equilibrium state inside the cell was achieved. The equilibrium partial pressure of CO₂ in the equilibrium cell, P_{CO_2} is calculated as

$$P_{CO_2} = P_T - P_V \tag{2}$$

The moles of remaining CO₂ in the gas phase at equilibrium condition, $n_{CO_2}^g$ was determined from

$$n_{CO_2}^g = \frac{V_g P_{CO_2}}{Z_{CO_2} RT} \tag{3}$$

Where V_g denote the vapor phase volume in the cell corrected with the consideration of liquid volume change caused by the

solubility of carbon dioxide, Z_{CO_2} is the compressibility factor of CO₂ in the gas-phase and T is the equilibrium temperature of

the cell. The moles of CO₂ in the liquid phase, $n_{CO_2}^l$, was obtained by relation 4.

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$$n^l_{CO_2} = n_{CO_2} - n^g_{CO_2} \qquad (4)$$

At the end, the CO_2 loading in the liquid phase, molality of the loaded CO_2, was calculated as

$$m_{CO_2} = \frac{n^l_{CO_2}(mol)}{w_{solvent}(kg)} \qquad (5)$$

4.2. CO₂ solubility tests results and discussion

First the results of our experiments were compared with the data on literature to calibrate and validate the apparatus. The solubility of CO_2 in aqueous solution of MDEA (2.00 kmol/m^3) at 25, 40, and 70°C was measured and compared with literature data in Figure 7 [18]. As shown in this figure, there is a good agreement between our work and the data available in the literature. So, accuracy of our data and the experimental procedure were validated.

Then, these measurements were repeated for aqueous solution of 40wt% MDEA with 0.2 wt% of UiO-66-NH₂. The CO_2 solubility in MDEA and MDEA with 0.2% UiO-66-NH₂ is shown in Tables1 and 2. Results represent that decreasing temperature improved the amine capacity in CO_2 uptake. Figures 8 and 9 shows that increasing pressure increases the CO_2 solubility in amine. Also, the results showed that addition of 0.2 wt% UiO-66-NH₂ nanoparticle to amine solution increases the CO_2 solubility up to 19.35% in 303.15 and 313.15 K, 20.09% in 323.15K and 20.9% in 333.15 K. Figures 8 and 9 show that increasing the system's temperature (10ºC) in different pressures; decrease the CO_2 solubility up to 4%.

The enhancement of CO_2 solubility in the presence of UiO-66-NH₂ nanoparticle can be explained as follows. MDEA is tertiary amine that has no labile hydrogen and then it cannot form a carbamate with CO_2 like primary and secondary amines. The reaction between tertiary amine and CO_2 described with base catalyzed reaction of CO_2 hydration [19-22].

Table1. CO₂ solubility in 40wt % MDEA solution

Pressure (kPa)	m_{CO_2}			
	303.15 (K)	313.15 (K)	323.15 (K)	333.15 (K)
	40 % mass MDEA solution			
183.33	2.830			
629.42	3.382			
1072.74	3.636			
1486.42	3.768			
2155.89	3.877			
291.90		2.823		
724.88		3.283		
1177.17		3.443		
1878.35		3.654		
2264.46		3.715		
138.71			2.156	
492.41			2.812	
919.87			3.108	
1341.83			3.254	
2158.84			3.399	
208.37				1.852
468.99				2.453
928.86				2.856
1376.32				3.074
2200.24				3.226

Table2. CO$_2$ solubility in 40wt % MDEA + 0.2 % UiO-66-NH$_2$ mixture

Pressure (kPa)	m_{CO_2}			
	303.15 (K)	313.15 (K)	323.15 (K)	333.15 (K)
40 % mass MDEA + 0.2 % UiO-66-NH$_2$ mixture				
187.25	3.572			
553.22	4.014			
1220.73	4.371			
1800.08	4.607			
2251.80	4.725			
150.62		3.013		
489.37		3.614		
1002.48		4.055		
1684.15		4.322		
2235.22		4.530		
200.29			2.911	
528.69			3.456	
1025.74			3.857	
1533.25			4.162	
2196.36			4.372	
188.33				2.322
632.35				3.215
1100.21				3.684
1666.32				3.910
2251.84				4.133

$$R_2NCH_3 + H_2O + CO_2 \leftrightarrow HCO_3^- + R_2 NHCH_3^+ \qquad (6)$$

According to zwitterion mechanism, the reaction of MDEA with CO$_2$ in liquid film, contain two reactions as follows:[20]

$$R_2R'N \ + CO_2 \rightarrow R_2R'NCOO \qquad (7)$$

$$R_2R'NCOO \ + H_2O \leftrightarrow HCO_3^- + R_2 R'NH^+ \qquad (8)$$
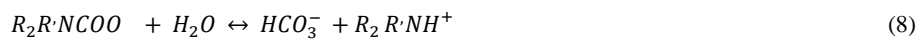
In reaction (7), $R_2R'NCOO$ is an unstable complex then the hydration reaction (8) take place in liquid phase. Generally the reaction between MDEA and CO$_2$ is not a fast reaction. When UiO-66-NH$_2$ added to MDEA as an activator, may react with CO$_2$ in liquid film and form an intermediate as follow:

$$UiO\_66\_NH_2 + CO_2 \rightarrow UiO\_66\_NH_2\,COO \qquad (9)$$
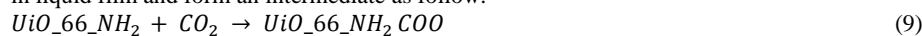
This reaction is a rapid reaction; the hydrolytic reaction of $UiO\_66\_NH_2\,COO$ in the liquid phase has been done as follow:

$$UiO\_66\_NH_2\,COO + H_2O \leftrightarrow UiO\_66\_NH_3^+ + HCO_3^- \qquad (10)$$
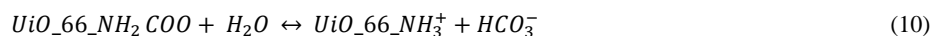
The intermediate $UiO\_66\_NH_2\,COO$ can transfer CO$_2$ to MDEA.

$$UiO\_66\_NH_2\,COO + R_2R'N \ \leftrightarrow UiO\_66\_NH_2 + R_2R'NCOO \qquad (11)$$
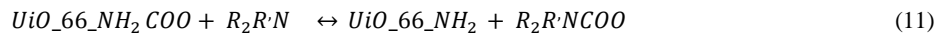
According to this reaction $UiO\_66\_NH_2\,COO$ can be renewed to $UiO\_66\_NH_2$.

The UiO-66-NH$_2$ in MDEA solution acts as a promoter and accelerates the absorption reaction.

Conclusions

Amino-functionalized Zr-MOF was synthesized with solvothermal method and characterized by XRD, IR, TGA, TEM and BET. The solubility of carbon dioxide in the aqueous solution of 40wt% N-Methyldiethanolamine MDEA measured by using a static high pressure equilibrium cell at different temperatures and carbon dioxide pressures up to 2300 kPa. Then, these measurements were repeated for aqueous solution of 40wt% MDEA with 0.2 wt% of UiO-66-NH$_2$. Results showed that increasing pressure and decreasing temperature, improves the amine capacity in CO$_2$ uptake and addition of UiO-66-NH$_2$ nanoparticle as an effective activator to MDEA solution increases the CO$_2$ solubility up to about 20%.
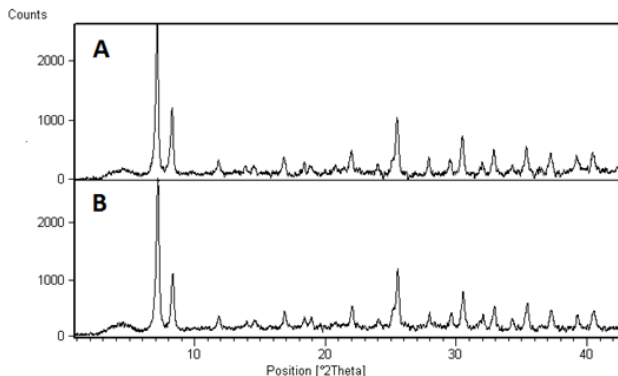
Figure 1. PXRD pattern of synthesized UiO-66-NH$_2$, A: as synthesized (before mixing with water), B: after 10 days mixing with water
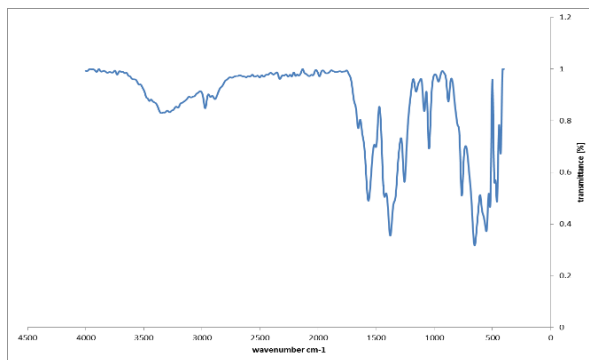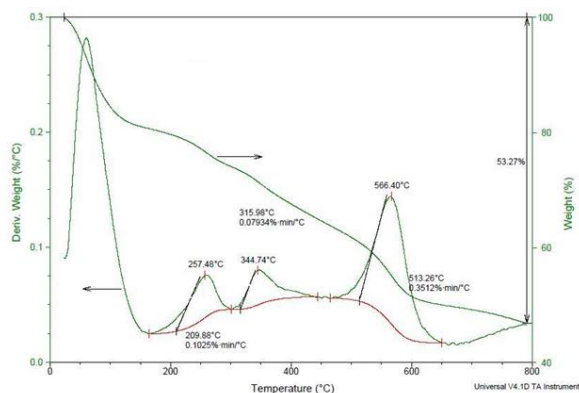

Figure 2. IR spectrum of UiO-66-NH$_2$
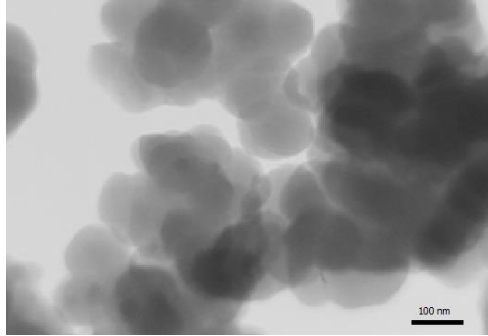

Figure 3. TG analysis of UiO-66-NH$_2$

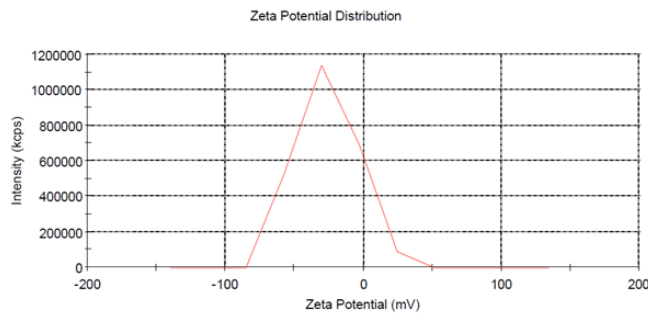**Figure4**. TEM analysis of UiO-66-NH$_2$

Figure 5. Zeta potential diagram for the nanofluid of 0.1 wt.% UiO-66-NH$_2$ in aqueous MDEA
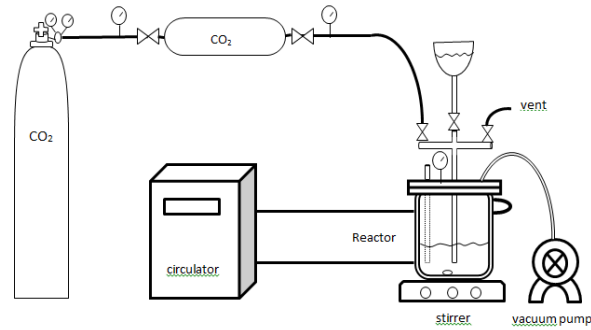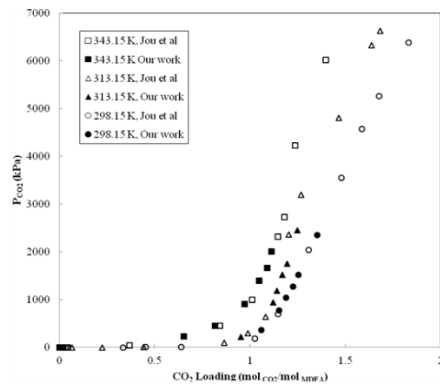

Figure 6. Experimental setup

Figure 7. Comparing the solubility data of CO_2 for 2.00 kmol/m³ MDEA solution at three given temperatures from this work and Jou et al [18]
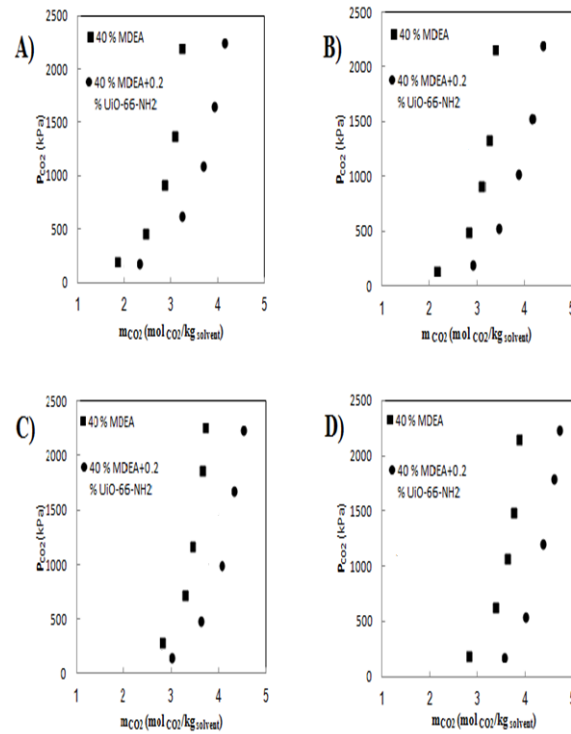

Figure 8. Comparison of solubility data of CO_2 for 40 wt % MDEA solution and 40 % wt MDEA + 0.2 % wt UiO-66-NH₂ nanofluid at different temperatures: A)333.15 K, B)323.15 K, C)313.15 K, D)303.15 K.
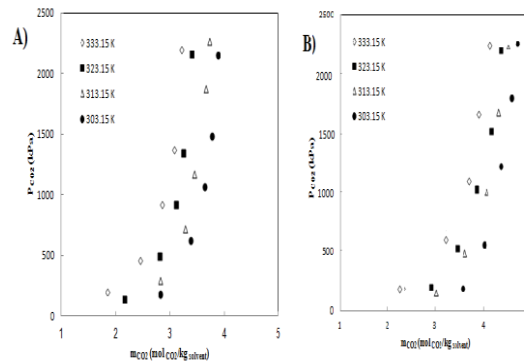

Figure 9. Comparison of solubility data of CO_2 at different temperatures;
A) 40 wt % MDEA solution; B) 40 % wt MDEA + 0.2 % wt UiO-66-NH₂ nanofluid

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